

CLAIMS

1. A method for rinsing metallized semiconductor substrates with an aqueous medium comprising including in said aqueous medium an amount effective to minimize metal corrosion of an anti-corrosive agent selected from organic carboxylic acids, organic nitrogen-containing compounds, inorganic acids other than nitric and carbonic acids, carbon monoxide and ozone, and mixtures of said anticorrosive agents.
2. A method according to claim 1 in which the anti-corrosive agent is selected from organic mono- and polycarboxylic acids and mixtures thereof.
3. A method according to claim 2 in which the anti-corrosive agent is selected from undecanedioic acid, dodecanedioic acid, sebacic acid, oxalic acid, citric acid, ascorbic acid, acetic acid and mixtures thereof.
4. A method according to claim 3 in which the anti-corrosive agent comprises acetic acid undecanedioic acid, dodecanedioic acid, sebacic acid, or mixtures of any two or all three of them.
5. A method according to claim 4 in which the substrate contains metallized copper.
6. A method according to Claim 1 in which the anti-corrosive agent is selected from nitrogen-containing organic compounds and mixtures thereof.
7. A method according to claim 6 in which the anti-corrosive agent comprises one or more nitrogen-containing cyclical organic compounds in which the nitrogen is contained in a ring.
8. A method according to claim 7 in which the anti-corrosive agent comprises benzotriazole, imidazole, benzamidazole, tolyltriazole,

tris(hydroxymethyl)aminomethane, ethanolamine carbonate or a mixture of two or more of them.

5 9. A method according to claim 8 in which the substrate contains metallized copper.

10 10. A method for rinsing metallized semiconductor substrates containing copper with an aqueous medium comprising including in said aqueous medium an amount of acetic acid effective to minimize metal corrosion of the copper.

15 11. A method for rinsing metallized semiconductor substrates containing titanium nitride with an aqueous medium comprising including in said aqueous medium an amount of acetic acid effective to minimize metal corrosion of the titanium nitride.

20 12. A method for rinsing metallized semiconductor substrates containing titanium nitride with an aqueous medium comprising including in said aqueous medium an amount of nitric acid effective to minimize metal corrosion of the titanium nitride.

25 13. A system for rinsing a metallized semiconductor substrate with an aqueous medium comprising means for contacting the substrate with said aqueous medium containing one or more anti-corrosive chemical agents wherein the concentration of the anticorrosive chemical agent or agents is maintained at a controlled level or within a predetermined range, and the substrate is maintained in contact with the chemical agent or agents for a predetermined time.

30 14. A system according to claim 13 comprising

a) a source of deionized water or other aqueous media for use as a rinse liquid,

5           b) a source of an anti-corrosive chemical agent or agents,

c). a container for conducting said rinsing,

d). means for introducing the deionized water into the container,

10           e). means for introducing the anti-corrosive chemical agent or agents into the container so as to maintain the concentration of anti-corrosive chemical agent in the container at a predetermined level or within a predetermined range, and

            f). means for maintaining the substrate in contact with deionized water containing the anti-corrosive chemical agent for a predetermined time.

15           15.     A system according to claim 14 in which the means for maintaining the concentration of the anti-corrosive chemical agent in a controlled manner comprise automated means.

20           16.     A system according to claim 13 in which the anti-corrosive chemical agent is selected from organic compounds, inorganic compounds other than nitric acid, mixtures of said organic compounds, mixtures of said inorganic compounds, mixtures of said organic and inorganic compounds, carbon monoxide, and ozone.

25           17.     A system according to claim 14 in which the anti-corrosive chemical agent is selected from organic compounds, inorganic compounds, mixtures of organic compounds, mixtures of inorganic compounds, mixtures of organic and inorganic compounds, carbon dioxide, carbon monoxide, and  
30           ozone.

18. A system according to claim 14 in which the anti-corrosive chemical agent comprises one or more organic compounds.

5 19. A system according to claim 18 in which the anti-corrosive chemical agent comprises one or more organic acids.

20. A system according to claim 19 in which the anti-corrosive chemical agent comprises acetic acid

10 21. A system according to claim 20 in which the semiconductor substrate contains metallized copper.

15 22. A system according to claim 20 in which the semiconductor substrate contains titanium nitride.

23. A system according to claim 13 in which the anti-corrosive chemical agent comprises acetic acid, undecanedioic acid, sebacic acid, dodecanedioic acid, or mixtures of any two or all three of them.

20 24. A system according to claim 23 in which the semiconductor substrate contains metallized copper.

25 25. A system according to claim 14 in which the anti-corrosive chemical agent comprises acetic acid, undecanedioic acid, sebacic acid, dodecanedioic acid, or mixtures of any two or all three of them.

26. A system according to claim 25 in which the semiconductor substrate contains metallized copper.

30 27. A system according to claim 13 in which the anti-corrosive chemical agent is selected from nitrogen-containing organic compounds in

which the nitrogen is contained in a ring; tris(hydroxymethyl)aminomethane, ethanolamine carbonate and mixtures thereof.

5 28. A system according to Claim 27 in which the anti-corrosive chemical agent is selected from nitrogen-containing organic compounds in which the nitrogen is contained in a ring; and mixtures thereof.

10 29. A system according to claim 28 in which the anti-corrosive chemical agent comprises benzotriazole, imidazole, benzamidazole, tolyltriazole, tris(hydroxymethyl)aminomethane, ethanolamine carbonate or a mixture of two or more of them.

15 30. A system according to claim 29 in which the semiconductor substrate comprises metallized copper.

31. A system according to claim 13 in which the anti-corrosive chemical agent comprises one or more inorganic acids.

20 32. A system according to claim 14 in which the anti-corrosive chemical agent comprises one or more inorganic acids.

33. A system according to claim 32 in which the anti-corrosive chemical agent comprises nitric acid.

25 34. A system according to claim 33 in which the semiconductor substrate contains titanium nitride.

30 35. A system according to claim 13 in which the anti-corrosive chemical agent comprises a mixture of organic and inorganic compounds.

36. A system according to claim 13 in which the semiconductor

substrate contains metallized aluminum and/or aluminum alloys.

37. A system according to claim 13 in which the semiconductor substrate contains metallized copper.

38. A system according to claim 13 in which the means for introducing the anti-corrosive chemical agent comprises automated means for maintaining the concentration of the anti-corrosive chemical agent in the container at a predetermined level or within a predetermined range.

39. A system according to claim 14 in which the means for introducing the anti-corrosive chemical agent comprises automated means for maintaining the concentration of the anti-corrosive chemical agent in the container at a predetermined level or within a predetermined range.

40. A system according to claim 38 in which the concentration of the anti-corrosive chemical agent in the container is maintained by measuring the conductivity of a recirculating loop comprising deionized water and the anti-corrosive chemical agent, and adding additional anti-corrosive chemical agent as needed in order to maintain the conductivity of the liquid in a circulating loop at a predetermined level or within a predetermined range.

41. A system according to claim 38 in which the means for introducing the anti-corrosive chemical agent into the container comprises a metering pump with preset stroke length and/or frequency.

42. A system according to claim 14 further comprising:  
means for subsequently rinsing the semiconductor substrate with deionized water, or other aqueous media alone.

43. A system according to claim 42, further comprising:

means for introducing a drying vapor into the container for drying the substrate.

5        44.     A method for rinsing metallized semiconductor substrates comprising: contacting the substrate with an aqueous medium containing one or more anti-corrosive chemical agents wherein the concentration of the anticorrosive chemical agent or agents is maintained at a controlled level or within a predetermined range, and the substrate is maintained in contact with the  
10     chemical agent or agents for a predetermined time.

15        45.     A method for rinsing metallized semiconductor substrates comprising;  
             a.     contacting the substrate with an aqueous rinse medium containing anti-corrosive chemical agent selected from organic compounds, inorganic compounds, carbon dioxide, carbon monoxide and ozone; and mixtures thereof; wherein the amount of the anticorrosive chemical agent in the aqueous medium is maintained in a  
20     controlled manner, at a predetermined concentration or within a predetermined range,  
             b.     conducting the rinse of step a for a predetermined time, and  
             c.     then rinsing the substrate with deionized water, or other  
25     aqueous media alone.

30        46.     A method according to claim 44 in which the anti-corrosive chemical agent is selected from organic compounds, inorganic compounds other than nitric acid, mixtures of said organic compounds, mixtures of said inorganic compounds, mixtures of said organic and inorganic compounds, carbon monoxide, and ozone.

47. A method according to claim 45 in which the anti-corrosive chemical agent is selected from organic compounds, inorganic compounds, mixtures of organic compounds, mixtures of inorganic compounds, mixtures of organic and inorganic compounds, carbon dioxide, carbon monoxide, and ozone.

48. A method according to claim 47 in which the anti-corrosive chemical agent comprises one or more organic compounds.

49. A method according to claim 48 in which the anti-corrosive chemical agent comprises one or more organic acids.

50. A method according to claim 48 in which the anti-corrosive chemical agent comprises acetic acid

51. A method according to claim 50 in which the semiconductor substrate contains metallized copper.

52. A method according to claim 50 in which the semiconductor substrate contains titanium nitride.

53. A method according to claim 44 in which the anti-corrosive chemical agent comprises acetic acid, undecanedioic acid, sebacic acid, dodecanedioic acid, or mixtures of any two or all three of them.

54. A method according to claim 53 in which the semiconductor substrate contains metallized copper.

55. A method according to claim 45 in which the anti-corrosive chemical agent comprises acetic acid, undecanedioic acid, sebacic acid,



dodecanedioic acid, or mixtures of any two or all three of them.

56. A method according to claim 55 in which the semiconductor substrate contains metallized copper.

57. A method according to claim 44 in which the anti-corrosive chemical agent is selected from nitrogen-containing organic compounds in which the nitrogen is contained in a ring; tris(hydroxymethyl)aminomethane, ethanolamine carbonate and mixtures thereof.

58. A method according to Claim 57 in which the anti-corrosive chemical agent is selected from nitrogen-containing organic compounds in which the nitrogen is contained in a ring; and mixtures thereof.

59. A method according to claim 58 in which the anti-corrosive chemical agent comprises benzotriazole, imidazole, benzamidazole, tolyltriazole, tris(hydroxymethyl)aminomethane, ethanolamine carbonate or a mixture of two or more of them.

60. A method according to claim 59 in which the semiconductor substrate comprises metallized copper.

61. A method according to claim 44 in which the anti-corrosive chemical agent comprises one or more inorganic acids.

62. A method according to claim 45 in which the anti-corrosive chemical agent comprises one or more inorganic acids.

63. A method according to claim 61 in which the anti-corrosive chemical agent comprises nitric acid, phosphonic acid, sulfamic acid, or mixtures thereof.

64. A method according to claim 63 in which the semiconductor substrate contains titanium nitride.

5 65. A method according to claim 44 in which the anti-corrosive chemical agent comprises a mixture of organic and inorganic compounds.

66. A method according to claim 44 in which the semiconductor substrate contains metallized-aluminum and/or aluminum alloys.

10 67. A method according to claim 44 in which the semiconductor substrate contains metallized copper.

15 68. A method according to claim 45 further comprising selecting the anti-corrosive chemical agent in accordance with the metal or metals comprising the semiconductor substrate, to minimize corrosion of said metal or metals resulting from the rinsing.

20 69. A method according to claim 45 wherein the two rinsing steps are carried out in the same container.

70. A method according to claim 45 further comprising

25 drying the semiconductor substrate, subsequent to the second rinse step utilizing a drying vapor

30 71. A method according to claim 70 in which the drying vapor is one that condenses on the surface of the substrate and reduces the surface tension of any residual water, causing said residual water to flow off of the surface.

72. A method according to claim 70 in which the drying vapor is isopropanol.

73. A method according to claim 70 in which the rinsing and drying steps are carried out in the same container.

74. A method for rinsing non-metallized semiconductor substrates comprising: contacting the substrate with an aqueous medium containing one or more chemical agents selected from hydrofluoric acid, hydrochloric acid, nitrilotriacetic acid, EDTA, gettering agents, chelating agents and surfactants wherein the concentration of the chemical agent or agents is maintained at a controlled level or within a predetermined range, and the substrate is maintained in contact with the chemical agent or agents for a predetermined time.

75. A method for rinsing non-metallized semiconductor substrates comprising:

- a. contacting the substrate with an aqueous rinse medium containing one or more chemical agents selected from hydrofluoric acid, hydrochloric acid, nitrilotriacetic acid, EDTA, gettering agents, chelating agents and surfactants wherein the amount of the chemical agent or agents in the aqueous medium is maintained in a controlled manner, at a predetermined concentration or within a predetermined range;
- b. conducting the rinse of step a for a predetermined time,
- c. then rinsing the substrate with deionized water, or other aqueous media alone.

76. A method according to claim 74 in which the means for maintaining the concentration of the chemical agent or agents in a controlled manner comprise automated means.

77. A method according to claim 75 in which the means for maintaining the concentration of the chemical agent or agents in a controlled manner comprise automated means.

5

78. A method according to claim 44 in which the means for maintaining the concentration of the chemical agent or agents in a controlled manner comprise automated means.

10

79. A method according to claim 45 in which the means for maintaining the concentration of the chemical agent or agents in a controlled manner comprise automated means.

add a17